PATENT SPECIFICATION

1,083,618

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Date of Application and filing Complete Specification: April 14, 1965. *No. 16091/65*

Application made in France (No. 983778) on July 31, 1964.

Complete Specification Published: September 20, 1967.

Index at Acceptance:—B2 K (1A2, 3D, 6A, 6C, 7A3, 7AX, 7AY, 8D, 8F, 9G, 9J, 9Q8, 9Q9, 9Q10, 9QX, 9QY).

Int. Cl.:—B 65 d 25/14.

SEE ERRATA SLIP ATTACHED

COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in the Internal Lining Varnishes for Canned-food Tins

We, ETABLISSEMENTS J. J. CARNAUD & FORGES DE BASSEINDRE, a French Body corporate of 37, Rue de Surene, Paris 8e, France, do hereby declare the invention for

ERRATA

SPECIFICATION NO. 1,083,618

Page 1, line 56, *for* "reach" *read* "react"

Page 1, line 72, *for* "ion" *read* "tin"

THE PATENT OFFICE,
14th May 1968

D 103419/8

sent at the surface of the sheet metal reacts with the sulphurous compounds released during the sterilisation, causing the formation of stannous sulphide which is evidenced by "marmorization" or veining of the tin. These impart a brown-bluish appearance to the internal surface of the tin. In addition, the sulphuretted hydrogen may cause the formation of ferrous sulphide in powder form which forms black spots on the metal and equally spots the product.

In order to protect the internal surface of the tins as well as their contents against these "sulphurisation" phenomena. it is already known to apply a coating of varnish on the tinplate.

Different types of varnish have already been suggested for this purpose.

Firstly, non-pigmented varnishes tending to oppose traversal by sulphuretted hydrogen and/or mercaptans have been proposed. These varnishes have the disadvantage that they do not intercept the sulphuretted compounds released during the thermal degradation of the proteins; they form no more than a simple barrier.

Varnishes charged with aluminium powder, intended to form an opaque lining have been proposed. The [illegible] the varnish.

Although the varnishes in this last group thus give satisfaction in respect of fixing sulphurised degradation products released in the course of sterilisation, they have various shortcomings well known in the industry producing canned-food tins. In particular they impart a fatty or greasy taste to elusively flavoured products: they have poor resistance to the heat transmitted during the soldering of the tins with solders having a low ion content; and there is a danger of loss of adhesion on the tinplate base in case of contact with fatty products (for example meats and pastes).

In order to eliminate these shortcomings, it has already been attempted to create anti-sulphur varnishes based on synthetic binding agents, such as epoxy-phenolic resins, and epoxy-urea-formaldehyde resins: experience shows however that the reactivity of zinc oxide with sulphuretted compounds, which is excellent in oleo-resinous varnishes, becomes poor if non-existent, in the aforementioned synthetic binding agents.

It is a main object of the present inven-

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We, ETABLISSEMENTS J. J. CARNAUD & FORGES DE BASSEINDRE, a French Body corporate of 37, Rue de Surene, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to internal protective coatings for canned-food tins.

It is known that the thermal degradation of proteins of animal or vegetable origin leads to the formation of various sulphurous products, in particular mercaptans and sulphuretted hydrogen. This occurs in particular during the sterilization of protein-containing foods, conditioned in tinplate packages. The tin present at the surface of the sheet metal reacts with the sulphurous compounds released during the sterilisation, causing the formation of stannous sulphide which is evidenced by "marmorization" or veining of the tin. These impart a brown-bluish appearance to the internal surface of the tin. In addition, the sulphuretted hydrogen may cause the formation of ferrous sulphide in powder form which forms black spots on the metal and equally spots the product.

In order to protect the internal surface of the tins as well as their contents against these "sulphurisation" phenomena, it is already known to apply a coating of varnish on the tinplate.

Different types of varnish have already been suggested for this purpose.

Firstly, non-pigmented varnishes tending to oppose traversal by sulphuretted hydrogen and/or mercaptans have been proposed. These varnishes have the disadvantage that they do not intercept the sulphuretted compounds released during the thermal degradation of the proteins; they form no more than a simple barrier.

Varnishes charged with aluminium powder, intended to form an opaque lining have been proposed. The sulphurisation of the tin covered by a film of this kind is simply hidden by the aluminium. The sulphuretted compounds are not intercepted, the varnish merely hides the presence of stannous sulphide under the varnish.

Varnishes described as "anti-sulphur" varnishes formed by an oleo-resinous varnish with an addition of zinc oxide have been proposed. These compounds reach with the sulphuretted compounds and "fix" the latter in the form of zinc sulphide. This latter being white in colour like the oxide, there is no change in the appearance of the varnish.

Although the varnishes in this last group thus give satisfaction in respect of fixing sulphurised degradation products released in the course of sterilisation, they have various shortcomings well known in the industry producing canned-food tins. In particular they impart a fatty or greasy taste to elusively flavoured products; they have poor resistance to the heat transmitted during the soldering of the tins with solders having a low ion content; and there is a danger of loss of adhesion on the tinplate base in case of contact with fatty products (for example meats and pastes).

In order to eliminate these shortcomings, it has already been attempted to create anti-sulphur varnishes based on synthetic binding agents, such as epoxy-phenolic resins, and epoxy-urea-formaldehyde resins; experience shows however that the reactivity of zinc oxide with sulphuretted compounds, which is excellent in oleo-resinous varnishes, becomes poor if non-existent, in the aforementioned synthetic binding agents.

It is a main object of the present inven-

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tion to provide means for imparting anti-sulphur properties to synthetic resin varnishes, that is to say an aptitude to intercept the sulphuretted compounds released during the sterilisation of certain food products.

According to the present invention a tinplate food container internal protective coating comprises a synthetic resin varnish, and an additive agent which is zinc carbonate.

The Applicants have in fact discovered that whereas the zinc oxide incorporated in synthetic varnishes wholly or largely loses its aptitude of reacting with sulphurised compounds, zinc carbonate incorporated in the said varnishes does intercept the sulphurised compounds in the form of sulphides and this with excellent effectiveness.

Zinc oxide also has the following advantages:

— lack of toxicity,
— insolubility or very slight solubility in water, of the order of 0.0018 to 100 g of H_2O;
— maximum thermal stability during the stoving of the varnish normally at close to 200°C, since the temperature of decomposition of $ZnCO_3$ is approximately 300°C;
— an anion associated with the amphoteric metal does not to cause excessive increase in the weight proportion of pigment to binding agent in the film of varnish applied, and
— cost compatible with the application scheduled.

Finally, the conversion of the zinc carbonate into sulphide is not accompanied by visible changes, since the zinc carbonate introduced into the varnish is of the same colour as its sulphide.

Taking these conditions into account, the Applicants have found that zinc carbonate ($ZnCO_3$) yields excellent results if it is incorporated in a synthetic varnish as for example, epoxy-phenolic resins, such as those sold under the trade names "Stoner-Mudge 5061 C" and "Holden 1635", epoxy-urea-formaldehyde resins such as that sold under the trade name "Stoner-Mudge 2799 A", and butadiene resins such as those sold under the trade names "Budium RK 662" and "Buton", the combination between binding agent and zinc carbonate not representing a limitation of the invention.

The $ZnCO_3$ additive is dispersed in the synthetic varnish acting as a binding agent by the conventional processes of the paints and varnishes industry.

The dosage of $ZnCO_3$ to be added to the carrying varnish may be selected at will, it depends on the quantity of sulphurised compounds one wishes to fix, but the varnish will always predominate in the coating.

At the same time, or after adding the zinc carbonate, one may moreover add to the carrying varnish one or more other pigments or adjuvants in order to comply with certain special conditions. The term "synthetic resin varnish" used herein and in the appended claims therefore should not be construed as excluding pigmented coatings.

Herein the term "Stoner-Mudge" refers to Messers Stoner-Mudge of Pittsburg, USA, and "Holden" refers to Arthur Holden & Sons of Birmingham, while "Budium" is made by E. I. Du Pont de Nemours & Co. of USA and "Buton" is made by Esso-Standard of London, England.

In order that the invention may be more clearly understood some preferred embodiments in accordance therewith will now be described by way of example.

EXAMPLE 1

A dispersion of 5g. of finely crushed $ZnCO_3$ was produced in 100g. of a commercial epoxy-phenolic varnish containing 30% by weight of resin and whose epoxy-phenolic ratio amounted to 70/30. This dispersion was performed by a ball mill or with a small three-cylinder crusher or mill.

After adjustment of viscosity to the value of 50 to 60 seconds, Food No. 4, by ethyl glycol as diluent, the varnish thus prepared was applied to sheets of tinplate by a roller varnisher, then stoved. This operation had the purpose of evaporating the solvents and of causing the curing of the epoxy-phenolic resin.

Starting with sheets of tinplate thus varnished, tins were produced by the conventional methods of the industry for the production of metal packings or boxes.

In order to verify the resistance of this $ZuCO_3$ containing varnish against sulphuretted compounds, these tins were filled with split peas covered by a brine, then closed and sterilised thereafter for 90 minutes at 120°C. After cooling and storage for different periods, the tins were opened and drained of their contents. It was observed that there had been no sulphurisation subjacent to the tin, nor any formation of ferrous sulphide in the open spaces of the tin.

A second test carried out in parallel with the same epoxy-phenolic varnish, but lacking the zinc carbonate, demonstrated the appearance of sulphurisation sub-jacent to the tin, as well as the formation of ferrous sulphide in the free space of the tins produced from this second kind of varnished plate.

A third test, equally performed in parallel with the same epoxy-phenolic varnish, but this time employing the zinc oxide currently employed in the paints and varnishes industry, in the proportion of 5 g. of pigment to 100 g. of liquid varnish, demon-

strated the appearance of the same defects as those specified immediately above, when the tins were opened.

EXAMPLE 2

10 g. of finely crushed $ZnCO_3$ was dispersed in 100 g. of a commercial varnish based on butadiene (e.g. Budium RK662) containing 52% by weight of resin. This dispersion was produced by means of conventional devices such as a ball mill or small three-cylinder mill as in Example 1.

After adjustment of viscosity of a value of 50 to 60 seconds Food No. 4 by white spirit as diluent, this varnish was applied on sheets of tinplate as in Example 1. The present test was carried out as previously, and it was found that there was no sulphurisation sub-jacent to the tin, nor any formation of ferrous sulphide.

Example 3

6 g. of finely crushed $ZnCO_3$ was dispersed in 100 g. of a commercial varnish based on epoxy-urea-formaldehyde (e.g. Stonor-Mudge 2799A) containing 37% by weight of resin. This dispersion was performed as hereinabove; after adjustment the viscosity was 50 to 60 seconds Food No. 4 and the diluent was ethyl-glycol; and the test sequence was conducted in analogous manner. It was found that there was no sulphurisation sub-jacent to the tin, nor any formation of ferrous sulphide.

WHAT WE CLAIM IS:

1. A tin-plate food container internal protective coating comprising a synthetic resin varnish and an additive which is zinc carbonate.

2. A coating in accordance with Claim 1 substantially as hereinbefore described with reference to any of the Examples.

3. A process of protecting the interior of tinplate food containers comprising applying to the tinplate sheet from which the said containers are made and/or to the interior surface of the containers a protective coating comprising a synthetic resin varnish and an additive which is zinc carbonate.

4. A process of protecting the internal surfaces of tinplate food containers according to Claim 3, substantially as herein described with reference to any one of the Examples.

5. A tin plate food container coated with a coating according to Claim 1 or 2 by the process of Claim 3 or Claim 4.

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